PRODUCTION WASTES

UDC 666.295.4

PRODUCTION OF GLAZES BASED ON SPENT VANADIUM CATALYSTS

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Translated from *Steklo i Keramika*, No. 4, pp. 29 – 31, April, 2009.

It is shown that spent vanadium catalysts can be used to obtain fritted colored glazes. The technological parameters for the synthesis of glaze glasses in the borosilicate system using spent vanadium catalysts are investigated, and the physical – chemical parameters of the glazes are determined. Decorative glazes with straw-color, brown, and gray tones and lustrous, mat, and semi-mat finishes have been obtained.

Key words: borosilicate glass, spent vanadium catalysts, decorative glaze coatings

In the Republic of Belarus, the enterprises "Grodno Azot" JSC, "Gomel' Chemical Works" JSC, and others use vanadium catalysts (VCs) as a silica carrier to produce sulfuric acid at the stage of oxidation of SO_2 into SO_3. Only "Grodno Azot" JSC uses of the order of 100 tons VC in the load. Of the catalyst used, 20% lose activity every year and must be replaced. The main components of the spent vanadium catalysts (SVCs) are expensive, but at the present time SVCs are not reprocessed in Belarus. Deactivated VCs are stored and, when enough VC has accumulated, shipped to Russia for reprocessing at the expense of the enterprises. According to GOST 12.1.005 vanadium compounds are classified as class-2 and -3 hazardous materials. The solubility of SVC components and the long storage times prior to removal for reprocessing create the possibility of environmental contamination by chemically dangerous substances.

The existing different physical – chemical methods for reprocessing SVCs can be conventionally divided into pyro- and hydrometallurgical. Drawbacks of pyrometallurgical methods are energy and materials intensiveness, the use of high temperatures and pressures, complexity of the equipment, one-time use of corrosive oxidizing reagents (for example, Cl_2), and emission of substantial amounts of toxic gases into the atmosphere. Hydrometallurgical methods are more promising; they are based on processing a deactivated contact mass by water solutions of acids, alkalis, and salts. Processing of these solutions by leaching with different chemical reagents releases the main components of the SVCs or results in the production of raw material for the synthesis of VCs.

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On the other hand it is known [1, 2] that oxides of various *d* elements, including V_2O_5, are used to obtain colored glasses, glazes, and pigments. Colored glass and glazes containing such oxides are distinguished by their high decorative qualities. In addition, the presence of oxides of *d* elements in glass often substantially changes its physical properties. For example, the introduction of large quantities of V_2O_5 into glass makes the glass UV-penetrable. In the Republic of Belarus there are several glass works and ceramic enterprises where such glasses and glazes can be produced.

The most common colored coatings are pigmented coatings in which the color is obtained by introducing coloring oxides or heat-proof pigments. Ceramic pigments are heat-resistant inorganic compounds with different colors [2]. However, glazes melted together with oxide colorants are preferable, since the coating obtained in this case has more intense luster and is characterized by higher brightness and purity of color tone [1].

The use of vanadium compounds for obtaining glazes with high decorative qualities is well known [1, 3, 4]. In compounds with oxygen (oxides) vanadium exhibits oxidation from +2 to +5, and all oxides show intense color: V_2O_5 — orange, VO_2 — dark blue, V_2O_3 — black, VO — gray. Vanadium compounds with a more complex chemical composition possess color ranging from green to violet, and the pigments and glazes range from green to blue. The decorative quality of glazes is achieved either by the wide color range of pigments containing vanadium or by the formation of large crystals, which are easily seen with the naked eye, on the surface of a coating. The best colored crystalline glazes are obtained on the basis of the compositions $V_2O_5 – TiO_2 – CoO$, $V_2O_5 – MoO_3$, and $V_2O_5 – TiO_2 – ZnO$.

In summary, the published information shows that vanadium compounds have wide applications for obtaining glazes and pigments [1 – 4]. They can be synthesized by using V_2O_5 separated from SVCs as well as directly from SVCs, but there are no published data on the use of SVCs for such purposes. Consequently, our objective in the present work was to study the possibility of using spent vanadium catalysts to produce fritted colored glazes for decorating ceramic articles and to study the properties of the glazes obtained.

The SVCs are distorted grayish-yellow cylinders, approximately 2 cm high and about 0.6 cm in diameter, which prior to the investigation were comminuted in a planetary mill to 300 – 1000 nm particles and specific surface area 40 m^2/g. The composition of the wastes studied is as follows (%[2]): 43.39 O, 18.90 Si, 10.30 C, 10.20 S, 9.09 K, 4.20 V, 2.01 Na, as well as Al, Ca, Fe, Cu, and Zn (< 1%).

X-ray phase analysis of the SVC showed that its phase composition is represented by α quartz as well as sulfates, polysulfates, and vanadates of the metals listed above.

Differential-thermal analysis established that when SVCs are heated several stages of decomposition are observed together with endothermal effects with mass losses. The first effect with a maximum at 180°C corresponds to removal of physically bound water with 8% mass loss. The presence of a triple endo- effect in the temperature range 540 – 820°C with 16% mass loss is probably due to the decomposition of sulfates. No transformations are observed at higher temperatures.

Chemical analysis shows that SVC consists of 40.43% silicon dioxide and 13.86% alkali and alkali-earth metals. The content of vanadium oxides as colorants in SVCs is 7.49% in terms of V_2O_5. Such material can be used in glass making. Silicon dioxide is a glass former and is used as a main component of silicate glasses. To one extent or another, the oxides K_2O, Na_2O, CaO, V_2O_5, FeO, ZnO, CuO, and SO_3 act as fluxes which lower the melting temperature. The presence of Al_2O_3 increases the heat-resistance and chemical stability of the glasses and decreases proneness to crystallization. The presence of V_2O_5 decreases the viscosity and surface tension of silicate melts. In addition, V_2O_5 is a typical colorant in glass and gives rise to bright luminescence; it also acts as an opacifier [4].

On the basis of its composition the material under study can be represented in the form of the glass-forming system $R_2O – RO – V_2O_5 – Al_2O_3 – SiO_2$, which is of definite scientific interest, since the presence of vanadium oxide makes it possible to synthesize colored glasses and glassy coatings with diverse physical – chemical properties.

The experimental glasses were synthesized in the borosilicate system (amount of SVC introduced — 40 – 55%). The maximum content of boron oxide was 20%, SiO_2 at least 35%, Al_2O_3 — 6%, Na_2O — no more than 4%, and the total amount of CaO and MgO introduced was at least 5%. These oxides were introduced using natural initial components. Six experimental compositions were investigated to obtain glaze glasses.

Synthesis was conducted by melting mixes in 0.3 liter porcelain and corundum crucibles in a gas flame furnace at temperature 1420 ± 20°C with soaking at the maximum temperature for 2 h. The temperature was increased at the rate 200 K/h to 800°C and 300 K/h to the maximum temperature.

The experimental data showed that in our experimental system glass is synthesized quite easily in the temperature interval 1350 – 1420°C with soaking at the maximum temperature for 1.5 – 2 h. The silicate melts obtained are noncorrosive, which permits synthesis to be conducted in porcelain crucibles.

Analysis of the founding and production properties of the silicate melts of the glasses studied showed that their capability to form glass definitely depends on the content of alkali and alkali-earth metal oxides as well as B_2O_3. So, increasing the amount of sodium oxide in the experimental system improves the technological properties of the glasses obtained. Adding calcium and magnesium oxides to the glass composition likewise improves the founding properties.

The synthesized glasses are characterized by transparency, are black, and possess a lustrous surface. No crystallizing and opalescing glass was observed during production, showing that glazes of good quality can be obtained on the basis of the glasses studied.

Fritted glazes were prepared by introducing 5 – 7% “Granitik-Vesko” clay into a glaze suspension and wet grinding the glaze glass in a porcelain drum to 0.1 – 0.3% residue on a No. 0063 sieve. The parameters of the glaze suspension are: moisture content 38 – 40% and working density 1340 – 1360 kg/m^3. The glaze slip obtained was deposited by pouring on a ceramic substrate based on red clay with water absorption 15 – 18% after calcination at 1050°C.

Glazed ceramic slabs were heat-treated in a gradient furnace in the temperature range 600 – 1050°C with exposure for 1 h. The experimental results showed that up to 700 – 800°C (depending on the chemical composition of the glass) there is no spreading and vitrification of the coatings; the only thing that happens is that the glaze layer is baked onto the ceramic base. Glazes start to interact with the ceramic substrate at 720 – 820°C, and fusing occurs in the temperature range 880 – 1050°C. Thus, it has been established that coatings with different texture (lustrous, mat, semi-mat) and a wide color range (from gray to brown tones) with melting temperature 880 – 1050°C can be obtained on the basis of the experimental glasses.

The experimental samples with a glaze coating were fired in SNOL electric laboratory furnaces with a prescribed heat-treatment regime: temperature increased to maximum value in 2 h; soaking at the maximum temperature for 1 h; cooling articles at the rate 80 – 100 K/h to 700°C; subsequent natural cooling. The firing temperatures were 950, 1000, and 1050°C.

[2] Here and below — content by weight.

TABLE 1.

Composition	Glass properties				Glaze properties		
	density, kg/m^3	microhardness, Pa	CLTE at 300°C, 10^{-7} K^{-1}	softening onset temperature, °C	firing temperature, °C	luster, %	Mohs hardness
1	2469.38	5259	69.48	620	950	74	5
					1000	60	5
					1050	28	6
2	2444.93	5082	61.41	560	950	39	5
					1000	35	6
					1050	20	5
3	2420.71	4990	57.22	510	950	57	6
					1000	53	6
					1050	23	5
4	2548.87	5376	69.48	575	950	61	6
					1000	66	6
					1050	36	6
5	2526.30	5420	63.48	525	950	60	6
					1000	65	6
					1050	39	6
6	2620.42	5683	73.31	520	–	–	–

The results of the investigations of the physical – chemical properties of the glasses and glaze coatings are presented in Table 1.

The experiment performed in the present work established that glass with synthesis temperature 1350 – 1450°C and good founding and manufacturing properties can be obtained. As the SiO_2 content increases in the compositions and the amount of boron oxide decreases, the technical properties degrade somewhat as a result of an increase of the viscosity of the glasses. The CLTE of the glasses lies in the range $(57.22 – 73.31) \times 10^{-7}$ K^{-1}, the softening onset temperature is 510 – 620°C, the density is 2420 – 2620 kg/m^3, the microhardness is 4990 – 5683 MPa, and the glasses can be used to synthesize low-melting glazes. As a result of the non-corrosiveness of the silicate melts which are formed, synthesis is best conducted in porcelain crucibles at 1420 ± 20°C.

The comprehensive investigations of the physical – chemical process which results in the formation of glaze coatings base on the experimental glasses and the study of the structure and properties of the coatings established the following:

a glaze suspension with prolonged firing regimes (majolica articles) must contain an additive in the form of refractory clay — up to 5 – 7% (above 100%); a higher content of clay additive is undesirable because defects (pinholes) appear in the coating;

the optimal firing temperature range is 950 – 1050°C depending on the chemical (mix) composition;

firing at temperatures below 950°C results in glazes with unsatisfactory quality — inadequate spreading and luster, disruption of the continuity of the layer, bubbles, pinholes; deposition of the glaze on pre-fired samples made from mixes based on local red clays intensifies the color tone of the glazes;

the glazes are characterized by good coverage; they have straw-color, greenish-brown, and gray tones;

the texture of the glazes developed is different and varies from lustrous to mat, the luster of the coatings ranges from 23 to 74%, and the Mohs hardness is 5 – 6.

The investigations performed in the present work show that it is possible and desirable to use SVCs to make colored glazes for decorating glazed tiles, majolica, and articles made of artistic ceramic. Glazes synthesized on the basis of spent vanadium glazes will make it possible to decrease the cost of raw materials by discontinuing the use of expensive imported colorants and to solve in part the problem of salvaging wastes.

We thank our colleagues in the Department of Glass and Ceramic Technology at the Belarussian State Technological University for making it possible for us to perform the experiment.

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